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Process optimization for the production of bio-resins using de-polymerized lignin

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Process Optimization for the production of Bio-resins using de-polymerized Lignin

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Outline

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- Objectives
- Research Methodologies
- Key Results
- Summary/Conclusions
- Acknowledgements

Introduction: Background & Motivation

- Plywood adhesives: High strength and moisture resistance properties
- > 95% of phenol from petroleum-derived benzene
- Lignocellulosic biomass contains 30-40% lignin; a polyphenolic macromolecule
    - Thermochemical de-polymerization
- Major challenge: reduced reactivity

Introduction: Significance

- PF Manufacturing industry valued at $10 billion globally;

- US Department of energy: Increase of 23.7% in Compound Annual Growth Rate between 2009 and 2015 (SRI Consulting, 2010);

- Cost of PF resins varies from **US$ 1,500 to US$ 2,000 per metric ton, mainly due to the high and fluctuating cost of phenol;**

- Need for lower dependence on non-renewable feedstock and maximization of value of trees.

Objectives

- To produce bio-phenol formaldehyde (BPF) resole resins at varying lignin-to-phenol substitution ratios while maintaining high quality;
- Multi-objective optimization: To maximize the adhesive strength and minimize the curing temperature of the BPF resole resins

Research Methodologies

Parameter	**Variable**	**Level (-1)**	**Level (0)**	**Level(+1)**
Formaldehyde-to-phenol	x1	1.2	2.1	3
% Phenol substitution	x2	25	50	75
Molecular weight of de-polymerized Lignin (DL) (g/mol)	x3	700[1]	1,100[2]	11,000[3]

[1] Hydrolytic de-polymerization at 350°C & 45 min; [2] Hydrolytic de-polymerization at 300°C & 60 min; [3] Hydrolytic de-polymerization at 250°C & 45 min (Nubla Mahmood, 2012)

Phenolic Resole Synthesis Reactions

- Addition Reactions
  - Methylolation of phenolic units
- Condensation Reactions
  - Formation of Diethyl Ether Bridges

$$(Methylolated)\ Phenolic\ unit + (Methylolated)\ Phenolic\ unit$$
$$\longrightarrow Phenolic\ unit - \boxed{CH_2 - O - CH_2} - Phenolic\ unit + H_2O$$

  - Formation of Methylene Bridges

$$(Methylolated)\ Phenolic\ unit + (Methylolated)\ Phenolic\ unit$$
$$\longrightarrow Phenolic\ unit - \boxed{CH_2} - Phenolic\ unit + (CH_2O) + H_2O$$

Properties of Phenolic Resoles (Commercial)

Property	Value	Source/Notes
Viscosity	150-600 cP at 25^{o}C	A. Pizzi & Y. Jin (2010) For plywood applications
Solid Content	40-60%	Kopf
pH	7-13	A. Pizzi
Free formaldehyde	0.19-0.67	Generally low
Unreacted Phenol	5-15%	A. Pizzi
Molecular Weight (Mn)	1000-2000 g/mol	A. Pizzi
Shear Strength	>2.5 MPa	Institute for Research in Construction (2009)

Research Methodologies

Lignin De-polymerization

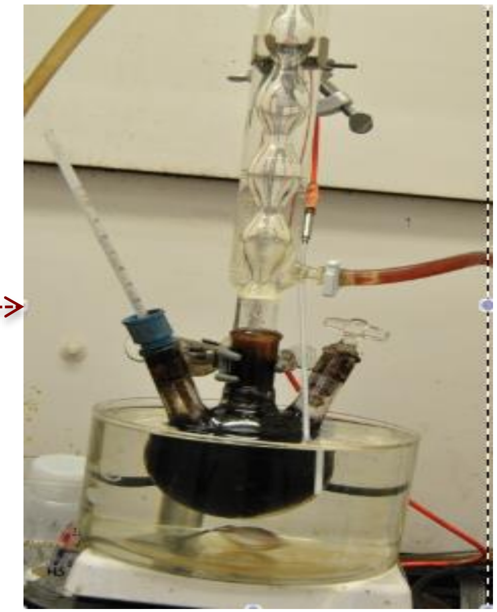
20 wt% Kraft Lignin (FP Innovations) at varying severities

Water
NaOH

22 bars

Final De-polymerized Lignin Product

BPF Resole Synthesis



Bio-Phenol Formaldehyde (BPF) resin:

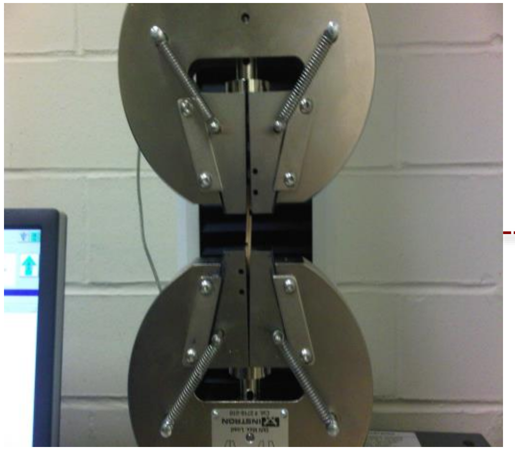
*De-polymerized Lignin
*Phenol
*Formaldehyde
*Water & Ethanol
*NaOH catalyst: 10 wt%

F:P ratio

Reaction for 2 h

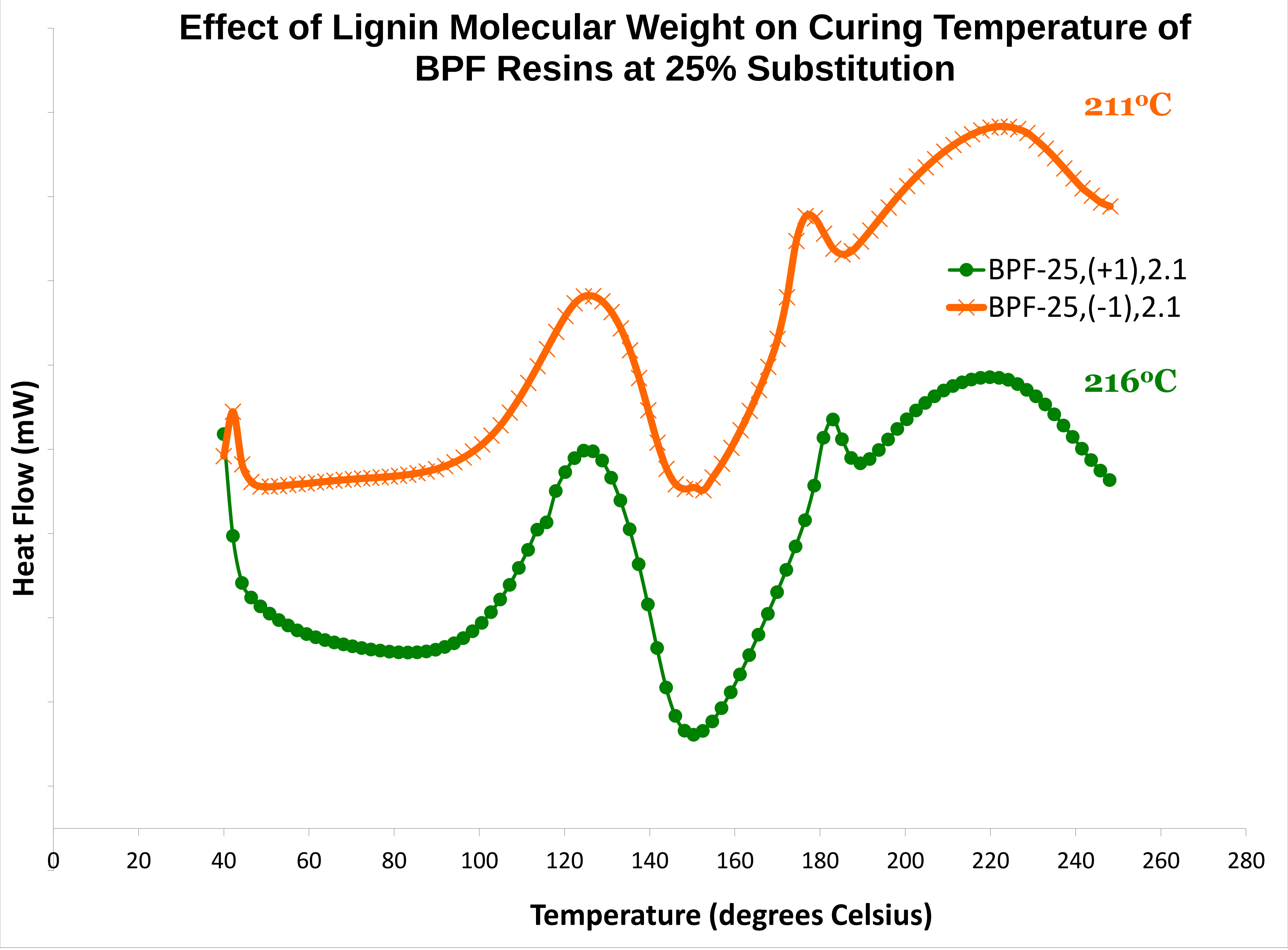
Research Methodologies – Analysis

Temperature: 180°C;
Pressure: 1.4 MPa;
Adhesive application (250 g/m²)

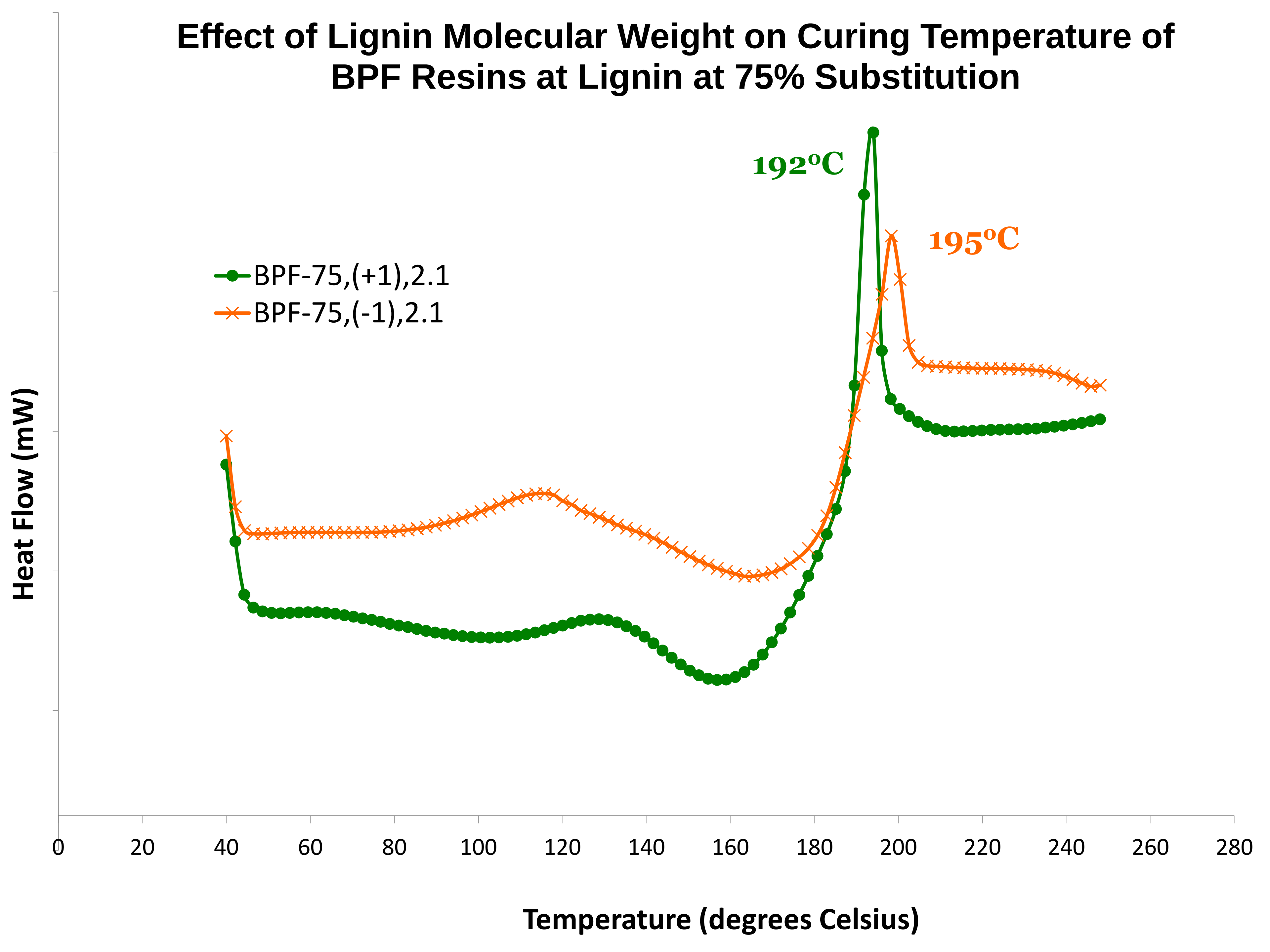


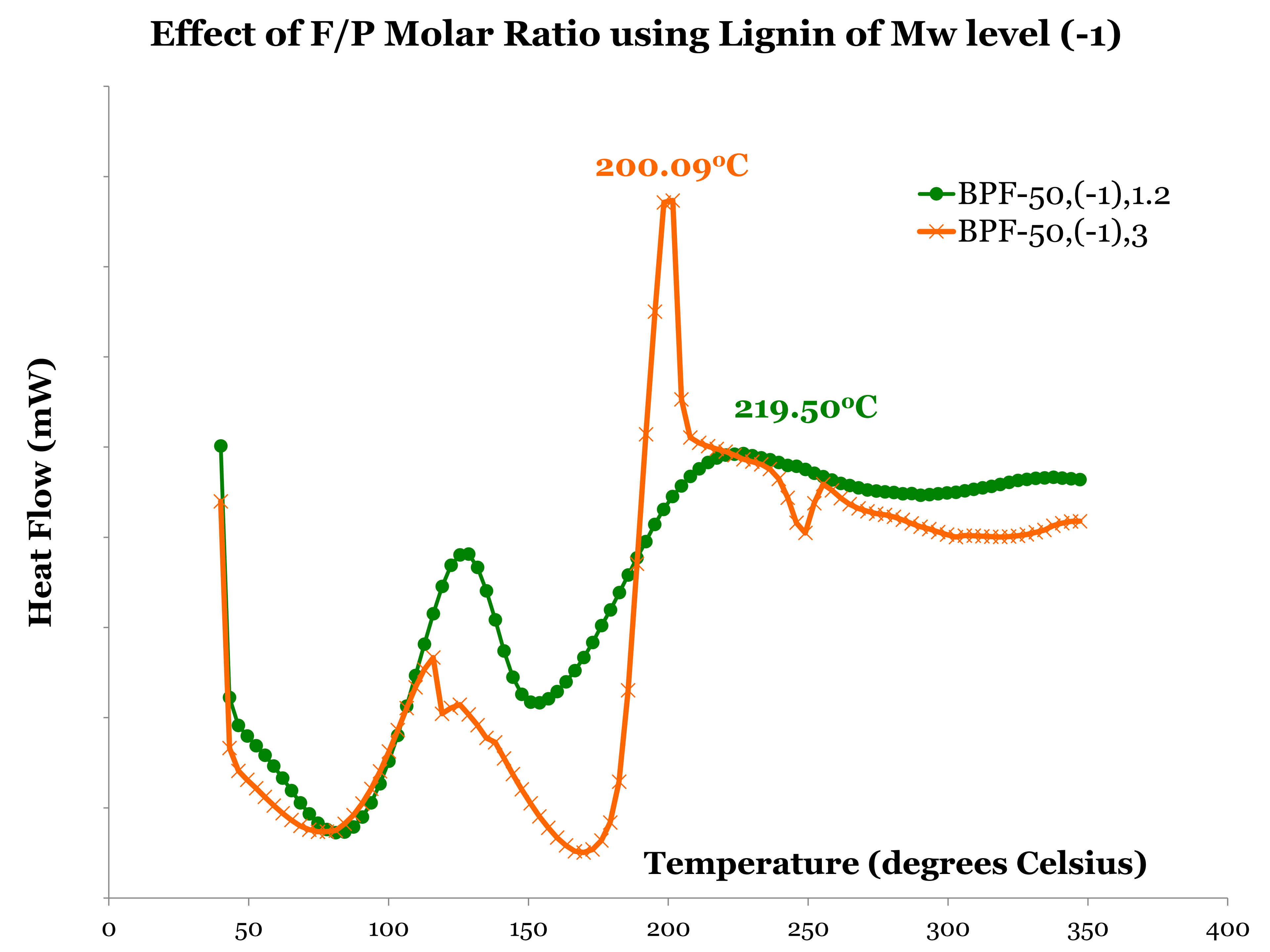
BPF Resoles - Viscosity

LABEL: BPF-%Substitution, Lignin Mw Level, F:P ratio		
Sample ID	**Viscosity (cP)**	**Standard Error**
BPF-25,(-1),2.1	26	(+/-) 1.2
BPF-50,(-1),1.2	229	(+/-) 8.5
BPF-50,(-1),3	165	(+/-) 7.2
BPF-75,(-1),2.1	191	(+/-) 3.5
BPF-25,(+1),2.1	124	(+/-) 0.4
BPF-50,(+1),1.2	288	(+/-) 0.8
BPF-50,(+1),3	137	(+/-) 1.2
BPF-75,(+1),2.1	348	(+/-) 0.6
BPF-25,(0),1.2	124	(+/-) 0.1
BPF-25,(0).3	16	(+/-) 0.1
BPF-50,(0),2.1	40	(+/-) 0.1
BPF-75,(0),1.2	>5,000	
BPF-75,(0)3	>5,000	

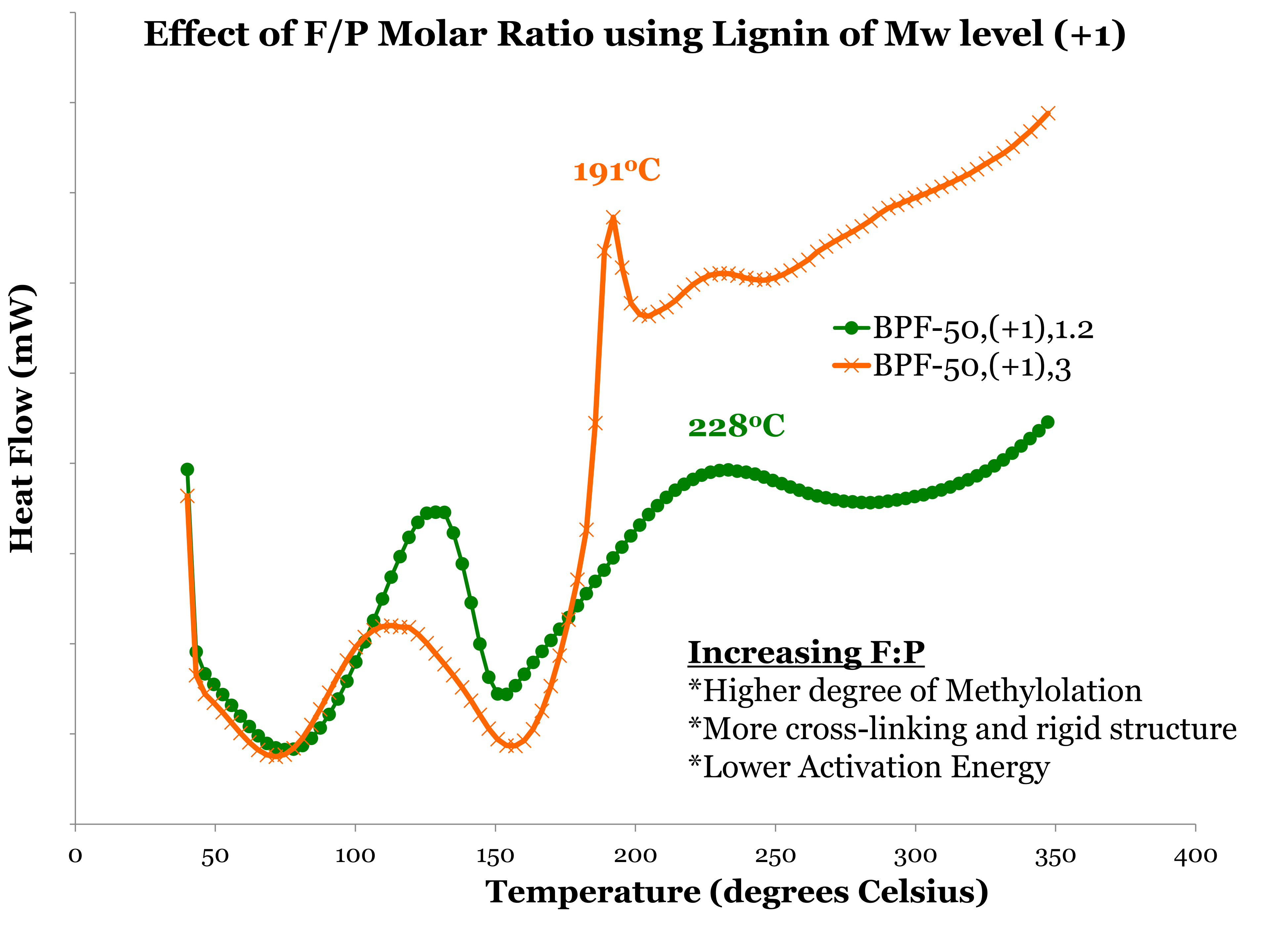


Effect of Lignin Molecular Weight on Curing Temperature of BPF Resins at 25% Substitution
211ºC
216ºC
BPF-25,(+1),2.1
BPF-25,(-1),2.1
Heat Flow (mW)
0
20
40
60
80
100
120
140
160
180
200
220
240
260
280
Temperature (degrees Celsius)


Effect of Lignin Molecular Weight on Curing Temperature of BPF Resins at Lignin at 75% Substitution
192°C
195°C
BPF-75,(+1),2.1
BPF-75,(-1),2.1
Heat Flow (mW)
0
20
40
60
80
100
120
140
160
180
200
220
240
260
280
Temperature (degrees Celsius)

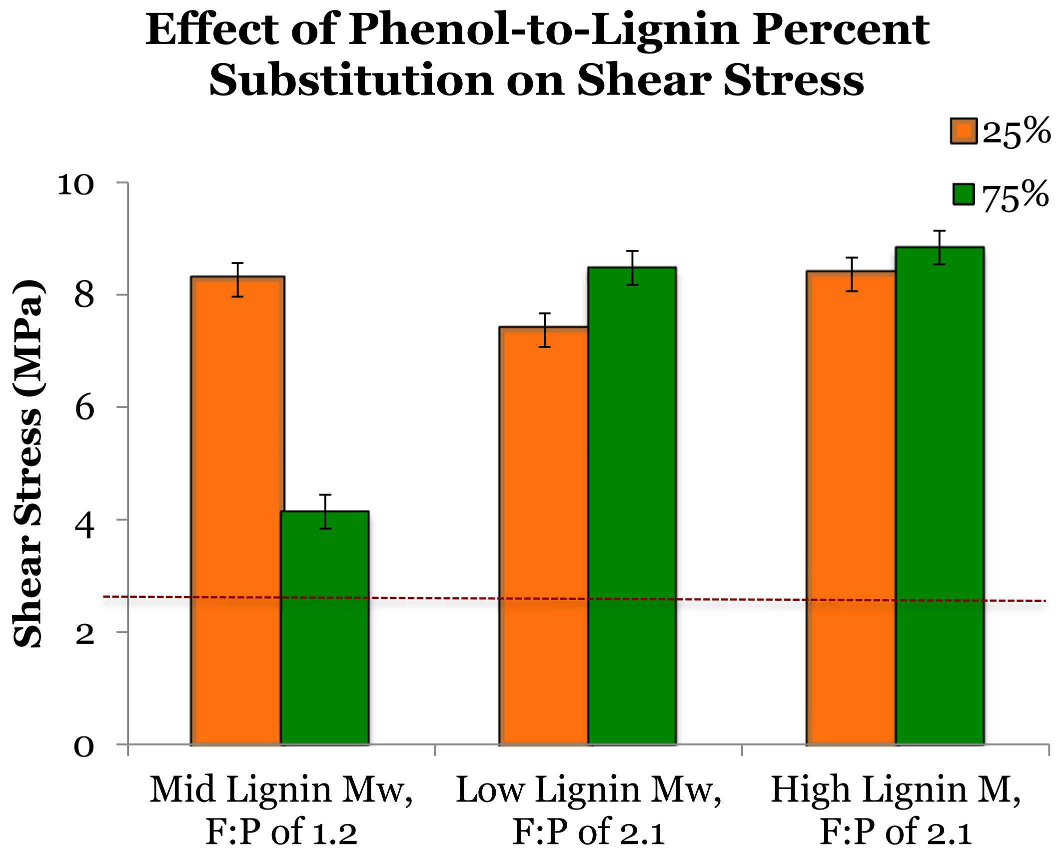


Effect of F/P Molar Ratio using Lignin of Mw level (-1)
200.09ºC
219.50ºC
BPF-50,(-1),1.2
BPF-50,(-1),3
Heat Flow (mW)
Temperature (degrees Celsius)
0
50
100
150
200
250
300
350
400



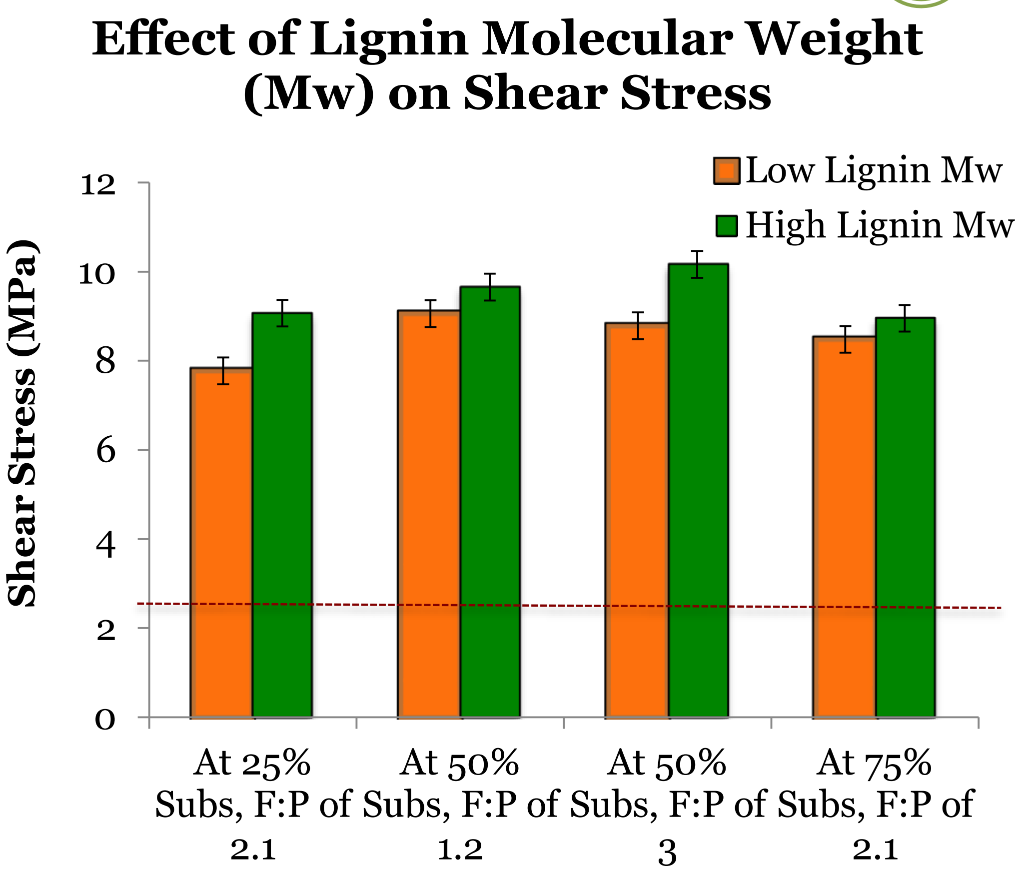
Effect of F/P Molar Ratio using Lignin of Mw level (+1)
191ºC
228ºC
BPF-50,(+1),1.2
BPF-50,(+1),3
Increasing F:P
*Higher degree of Methylolation
*More cross-linking and rigid structure
*Lower Activation Energy
Heat Flow (mW)
0
50
100
150
200
250
300
350
400
Temperature (degrees Celsius)

Effect of % Substitution



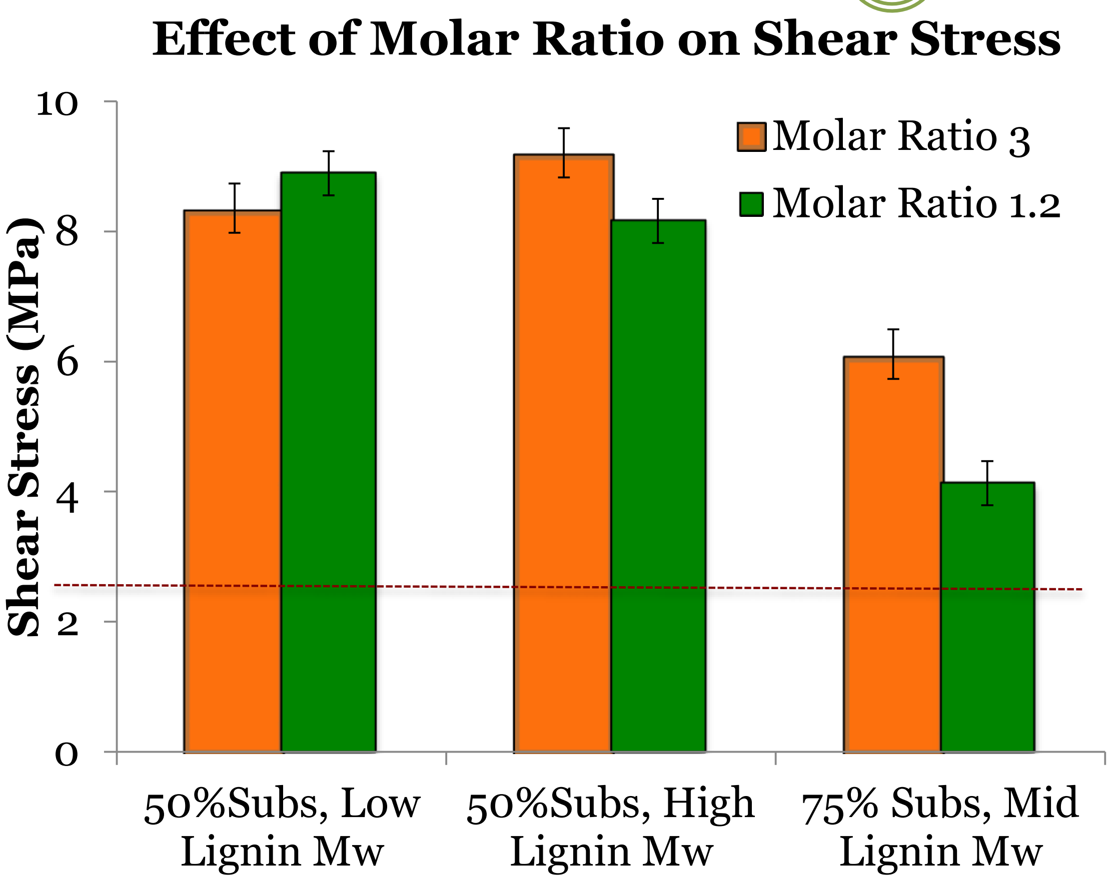
Curing Temperature: 180°C; Pressure: 1.4 MPa
Adhesive application (250 g/m²)

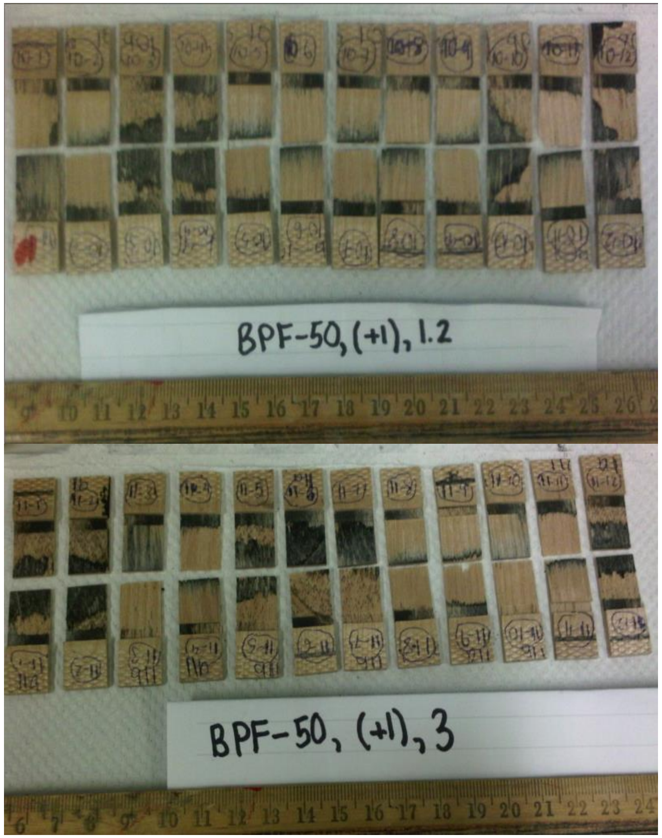
Effect of Lignin Mw



Curing Temperature: 180°C; Pressure: 1.4 MPa
Adhesive application (250 g/m²)

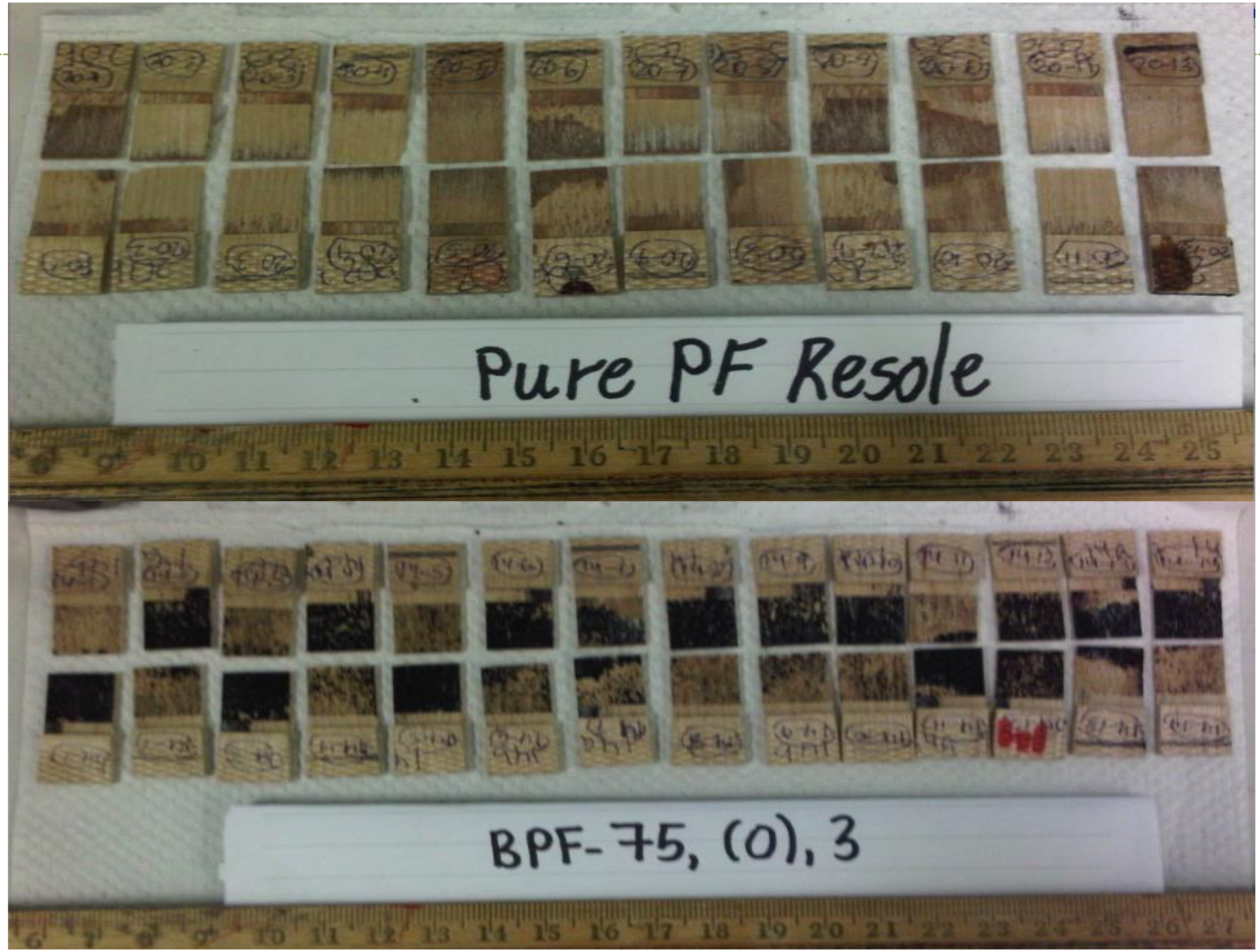
Effect of F:P Molar Ratio





Curing Temperature: 180°C; Pressure: 1.4 MPa
Adhesive application (250 g/m²)

Wood Failure (Qualitative)



Summary

- At low percent substitutions, BPF resole qualities are similar to those of pure PF resoles;
- Relevance of observing BPF qualities at high percent substitutions;
- High percent substitution: acceptable shear strength, lower wood failure, and exceedingly high viscosity measurements;
- Increasing F/P ratio reduces the curing temperature and increases the shear strength;
- Increasing Lignin Mw reduced the curing temperature and increases the shear strength while also increasing the viscosity.

Conclusions/Recommendations

- To obtain high-quality BPF resoles at higher % substitutions:
  - Increase lignin molecular weight; increase F/P ratio; control viscosities of BPF resoles.
- At 75%, lowest curing temperature (192^{o}C) and highest adhesive strength (9.0 MPa) obtained at high lignin Mw and F:P ratio of 2.1 (348 cp);
  - Pure PF resole: Curing temperature of ~150^{o}C and adhesive strength of 8.3 MPa
- GPC analysis to determine molecular weight of BPF resoles;
- TGA analysis to determine thermal stability of BPF resoles.

Acknowledgements

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